PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08L 23/10, 23/04, C08K 5/14 — A1

(11) International Publication Number: WO 96/20247

(43) International Publication Date: 4 July 1996 (04.07.96)

(21) International Application Number: PCT/NL95/00441

(22) International Filing Date: 21 December 1995 (21.12.95)

(30) Priority Data:
9401165 27 December 1994 (27.12.94) BE

(71) Applicant *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: REPIN, Johannes, Fredericus [NL/NL]; Klingbemden 177, NL-6441 KX Brunssum (NL). BRULS, Wilhelmus, Gerardus, Marie [NL/NL]; Graaf Wolterhoenstraat 32, NL-6234 BE Meerssen (NL). CHODÁK, Ivan [SK/SK]; Zubekova 9, 941 01 Bratislava (SK). CHORVÁTH, Igor [SK/SK]; Hanulova 2, 841 01 Bratislava (SK).

(74) Agent: SCHELTUS, Irma; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

(81) Designated States: CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
In English translation (filed in Dutch).

(54) Title: CROSS-LINKED POLYMER COMPOSITION CONTAINING A POLYPROPYLENE-ETHYLENE COPOLYMER AND AN ETHYLENE-α-OLEFIN COPOLYMER

(57) Abstract

The invention relates to a cross-linked polymer composition containing 40-90 wt.% propylene-ethylene copolymer with 8-20 wt.% ethylene and 10-60 wt.% ethylene-α-olefin copolymer with 75-90 wt.% ethylene and a density of 920-890 kg/m^3, having a notched Izod impact strength ≥ 10kJ/m^2 at -20 °C and a flexural modulus higher than 500 MPa. The cross-linked polymer composition is prepared by melting and kneading propylene-ethylene copolymer and ethylene-α-olefin copolymer in the presence of a radical forming agent, a cross-linking agent and, eventually a peroxide inhibitor.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

CROSS-LINKED POLYMER COMPOSITION CONTAINING A POLYPROPYLENE-ETHYLENE COPOLYMER AND AN ETHYLENE-α-OLEFIN COPOLYMER

The invention relates to a cross-linked polymer composition containing 40-90 wt.% propylene-ethylene copolymer and 10-60 wt.% ethylene-α-olefin copolymer.

A polymer composition of this type is known from DE-A-32,30,516.

Herein a cross-linked polymer composition is described containing propylene-ethylene copolymer and ethylene-α-olefin copolymer having a high impact resistance at low temperature and also has good flow properties.

A drawback of the polymer composition described above is that the stiffness of these products with a high impact resistance is too low.

The aim of the invention is to obtain a polymer composition that does not present the above drawback.

The invention is characteriezd in that the propylene-ethylene copolymer contains 8-20 wt.% ethylene, the ethylene-α-olefin copolymer contains 75-90 wt.% ethylene and has a density of 920-890 kg/m^3 and in that the polymer composition has a notched Izod impact strength $\geq$ 10 kJ/m^2 at -20°C and a flexural modulus of more than 500 MPa.

This ensures that the polymer composition is very suitable for use in moulded parts that have to show good impcat strength at low temperatures and also a high stiffness.

JP-A-61/85462 describes a cross-linked polymer composition containing 60-85 wt.% of a propylene-ethylene block copolymer and 15-40 wt.% of an ethylene-α-olefin random copolymer. This polymer composition has, as the polymer composition according to DE-A-32,30,516, a high

impact strength at low temperatures. The cross-linked polymer composition according to JP-A-61/85462 has as a drawback that the stiffness of this product is too low.

The stiffness of a polymer composition is reflected by the flexural modulus, determined according to ASTM D790.

The impact strength of a polymer composition is reflected by the notched Izod impact strength, determined according to ASTM D256.

With particular preference the polymer composition has a notched Izod impact strength $\geq$ 10 kJ/m^2 at -30°, determined according to ASTM D256.

When the polymer composition according to the invention is used in large moulded parts, such as car bumpers, it is also important that the polymer composition has good flow properties. Preferably the polymer composition has a viscosity of more than 550 Pa.s, determined according to ASTM D3835 at a shear rate of 115 s^{-1}. The cross-linked polymer composition according to the invention that has this viscosity can readily be thermoplastically processed.

The cross-linked polymer composition according to the invention contains 40-90 wt.% propylene-ethylene copolymer relative to the total amount of propylene-ethylene copolymer and ethylene-α-olefin cpolymer present. 'Propylene-ethylene copolymer' is within the context of this invention understood to mean: copolymers that containing 8-20 wt.% ethylene.

The compatibility of the propylene-ethylene copolymer with the ethylene-α-olefin copolymer is bad and the impact strength is low when the ethylene content in the ethylene-propylene copolymer is lower than 8 wt.%.

Examples of propylene-ethylene copolymers are: random copolymers of propylene, ethylene and an α-olefin containing 4-10 carbon atoms, block copolymers of propylene, ethylene and an α-olefin containing 4-10 carbon atoms, and reactor mixtures a propylene homopolymer and

ethylene homopolymer or ethylene copolymer containing ethylene and one or more α-olefins with 3-10 carbon atoms. Preferably the propylene-ethylene copolymer is a propylene-ethylene block copolymer.

Polymer compositions with the highest impact strength are obtained when a propylene-ethylene block copolymer is used in the polymer composition according to the invention.

The cross-linked polymer composition according to the invention also contains 10-60 wt.% ethylene-α-olefin copolymer relative to the total amount of propylene-ethylene copolymer and ethylene-α-olefin copolymer present. 'Ethylene-α-olefin copolymer' is in the context of this invention understood to mean random copolymers of ethylene with one or more olefinic comonomers containing 3-10 carbon atoms, containing 75-90 wt.% ethylene with a density of 920-890 kg/m^3.

The density of the ethylene-α-olefin copolymer is too low when the ethylene content in the ethylene-α-olefin copolymer is under 75 wt.%. Than also the stiffness of the crosslinked polymer composition decreases.

The stiffness of the cross-linked polymer composition decreases till under 500 MPa when the ethylene content of the ethylene-α-olefin copolymer is under 890 kg/m^3.

When the polyethylene has a density of more than 920 kg/m^3 the impact resistance of the polymer composition at low temperatures decreases.

Preferably 1-butene, 1-hexene and/or 1-octene are used as α-olefin in the ethylene-α-olefin copolymer.

Examples of ethylene-α-olefin copolymers are low-density polyethylene (LDPE), very-low-density polyethylene (VLDPE) and ultra-low-density polyethylene (ULDPE) and linear-low-density polyethylene (LLDPE).

The cross-linked polymer composition according to the invention can be prepared by kneading and melting a mixture of the propylene-ethylene copolymer and the

ethylene-α-olefin copolymer in the required ratio in the presence of a radical-forming agent and a cross-linking agent.

The radical-forming agent can be chosen from among peroxides or azo compounds. Preferably peroxides are used. Examples of peroxides are benzyl peroxide, t-butyl perbenzoate, t-butyl peracetate, t-butyl peroxyisopropylcarbonate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexyn-3, t-butyl diperadipate, t-butyl peroxy-3,5,5-trimethylhexanoate, methylethylketone peroxide, cyclohexanone peroxide, di-t-butyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyn-3, 1,3-bis-(t-butylperoxyisopropyl)benzene, t-butylcumyl peroxide, 1,1-bis-(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis-(t-butylperoxy)cyclohexane, 2,2-bis-(t-butylperoxy)-butane, p-menthane hydroperoxide, diisopropylbenzene hydroperoxide, cumene hydroperoxide, t-butyl hydroperoxide, p-cumene hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide and 2,5-dimethyl-2,5-di(hydroperoxy)hexane.

The amount of radical-forming agent present during the melting and kneading of the propylene-ethylene copolymer and the ethylene-α-olefin copolymer is usually between 0.01 and 3 wt.%, relative to the amount of propylene-ethylene copolymer plus ethylene-α-olefin copolymer. Preferably the amount of radical-forming agent is 0.05-2 wt.%, relative to the amount of propylene-ethylene copolymer plus ethylene-α-olefin copolymer.

The cross-linking agent can be chosen from the group comprising compounds containing dihydroxy, divinyl, diallyl or triallyl containing compounds, such as 1,2-, 1,3- and 1,4-dihydroxybenzene, divinyl benzene or diallylphthalate.

Preferably 1,4-dihydroxybenzene is used as the cross-linking agent.

An amount of between 0.001 and 3 wt.% cross-linking agent, relative to the amount of propylene-ethylene copolymer plus ethylene-α-olefin copolymer, is usually present during the melting and kneading of the propylene-ethylene copolymer and the ethylene-α-olefin copolymer. Preferably an amount of between 0.005 and 0.5 wt.% cross-linking agent is present.

Preferably a peroxide inhibitor is also present during the melting, kneading and mixing of the propylene-ethylene copolymer and the ethylene-α-olefin in the presence of a peroxide and a cross-linking agent. The peroxide inhibitor ensures that the cross-linking reaction does not take place immediately when the melting and kneading are started. That way a good degree of mixing of the propylene-ethylene copolymer and the ethylene-α-olefin copolymer can be achieved before the cross-linking of the polymer composition takes place.

Various compounds may be used as the peroxide inhibitor, such as 1,4-dihydroxybenzene, 2,6-di-t-butyl-p-cresol, t-butylcatechol, 4,4'-butylidene-bis-(3-methyl-6-t-butylphenol), 2,2'-methylene-bis-(4-methyl-6-t-butylphenol), 4,4'-thio-bis(6-t-butyl-3-methylphenol), mercaptobenzothiazole, dibenzothiazoledisulphide, 2,2,4-trimethyl-1,2-dihydroquinone polymers, phenyl-β-naphthylamine, N,N'-di-β-naphthyl-p-phenylenediamine and N-nitrosodiphenylamine.

The amount of peroxide inhibitor present during the melting and kneading of the polypropylene and the polyethylene is 0-0.5 wt.%, relative to the amount of propylene-ethylene copolymer plus ethylene-α-olefin copolymer.

Preferably both the cross-linking agent and the peroxide inhibitor are 1,4-dihydroxybenzene and between 0.005 and 0.5 wt.% 1,4-dihydroxybenzene, relative to the amount of propylene-ethylene copolymer plus ethylene-α-olefin copolymer, is added.

The propylene-ethylene copolymer and ethylene-α-

olefin copolymer are kneaded and melted together with the radical-forming agent, the cross-linking agent and optionally the peroxide inhibitor in the usual equipment, such as mixers, kneaders and single- or twin-screw extruders. The temperature during the melting and kneading is 165 to 270°C.

The cross-linked polymer composition according to the invention may furthermore contain the usual additives such as fibres, fillers, nucleating agents, plasticizers, flame retardants, flow-promoting agents, lubricants, stabilisers and impact improving agents.

The cross-linked polymer composition according to the invention is suitable for use large injection moulded parts for the automotive industry that are exposed to low temperatures, such as bumpers.

The invention will be further elucidated with reference to examples without the invention being limited thereto.

Examples

Measuring methods

The impact strength (Izod) was determined according to ASTM D256.

The viscosity (SSV) was determined according to ASTM D3835 using a Göttfert 1500 Viscotester at a shear rate of 115 s^{-1} and a temperature of 240°C. The diameter of the capillary tube was 1 mm, its length 30 mm and the entry angle was 180°C. The measurement was started after the material had been melted for 6 min.

The melt index (MI) was determined according to ASTM D1238, at a temperature of 190°C and a pressure of 21.2 N.

The flexural modulus was determined according to ASTM D790.

The density was determined according to ASTM D792.

The materials used

Propylene-ethylene copolymer (PP):

A1) a propylene-ethylene block copolymer containing 9% ethylene.

A2) a propylene-ethylene block copolymer containing 12% ethylene.

A3) a propylene homopolymer

Ethylene-α-olefin copolymer (PE):

B1) VLDPE with 84 wt.% ethylene, a density of 911 kg/m^3 and an MI of 2.2 g/10 min.

B2) VLDPE with 89 wt.% ethylene a density of 919 kg/m^3 and an MI of 2.2 g/10 min.

B3) HDPE with 99.5 wt.% ethylene, a density of 952 kg/m^2 nd a MI of 10 g/10 min.

B4) ethylene-propylene-diene rubber with 65 wt.% ethylene and a density of 860 kg/m^2

B5) ethylene-propylene rubber with 71 wt.% ethylene, a density of 880 kg/m^2 and a MI of 0.4 g/10 min.

Radical-forming agent(R): Luperco 802PP40
Cross-linking agent (C): 1,4-dihydroxybenzene
Peroxide inhibitor (P): 1,4-dihydroxybenzene

Examples I-X and Comparative Experiments A-D

The polymer compositions were prepared by melting and kneading the various components in a Haake twin-screw extruder at a temperature of 175°C and a throughput of 20 g/min.

TABLE 1

Example	PP wt.%	PE wt.%	R wt.%	C+P wt.%	Izod (-20°C) kJ/m²	Izod (-30°C) kJ/m²	Izod (-40°C) kJ/m²	SSV Pa.s	Flexural Modulus MPa
I	A1/60	B2/40	1	0.1	12	7	3	548	680
II	A1/60	B2/40	1	0.2	13	8	5	798	780
III	A1/60	B2/40	1	0.05	10	-	-	483	665
IV	A1/60	B1/40	2	0.1	11	-	-	500	530
V	A1/60	B1/40	1	0.1	NF	7	5	628	615
VI	A1/60	B1/40	1	0.2	NF	10	5	658	670
VII	A1/60	B1/40	1	0.4	NF	16	5	1079	750
VIII	A2/60	B2/40	0.5	0.1	16	12	6	1079	785
IX	A2/60	B2/40	1	0.1	NF	18	5	867	640
X	A2/60	B1/40	1	0.1	NF	NF	7	841	585

NF = no fracture

TABLE 2

Comparative experiments A-H

Experiment	PP wt.%	PE wt.%	R wt.%	C+P wt.%	Izod (-20°C) kJ/m²	Izod (-30°C) kJ/m²	Izod (-40°C) kJ/m²	SSV Pa.s	Flexural Modulus MPa
A	A2/100	-	1	0.1	7	-	-	412	1050
B	-	B1/100	1	0.1	NF	NF	NF	2948	115
C	A1/60	B2/40	-	0.1	8	-	-	460	870
D	A2/60	B1/40	1	-	9	-	-	587	515
E	A3/60	B1/40	1	0.1	-	-	-	ND	650
F	A2/60	B3/40	1	0.1	5.5	-	-	ND	1040
G	A2/6-	B4/40	1	0.1	NF	NF	8.9	ND	360
H	A2/60	B5/40	1	0.1	NF	NF	NF	ND	320

NF = no fracture

ND = not determined

C L A I M S

1. Cross-linked polymer composition containing 40-90 wt.% propylene-ethylene copolymer and 10-60 wt.% ethylene-α-olefin copolymer, characterised in that the propylene-ethylene copolymer contains 8-20 wt.% ethylene, the ethylene-α-olefin copolymer contains 75-90 wt.% ethylene and has a density of 920-890 kg/m^3 and in that the polymer composition has a notched Izod impact strength ≥ 10 kJ/m^2 at -20°C and a flexural modulus of more than 500 MPa.
2. Cross-linked polymer composition according to Claim 1, characterized in that the polymer composition has a notched Izod impact strength ≥ 10 kJ/m^2 at -30°C.
3. Cross-linked polymer composition according to Claim 1 or Claim 2, characterized in that the polymer composition has a viscosity of more than 550 Pa.s.
4. Cross-linked polymer composition according to any one of Claims 1-3, characterized in that the propylene-ethylene copolymer is a propylene-ethylene block copolymer.
5. Cross-linked polymer composition according to any one of claims 1-4, characterised in that the α-olefin in the ethylene-α-olefin copolymer is 1-butene, 1-hexene and/or 1-octene.
6. Method for preparing the cross-linked polymer composition according to any one of Claims 1-5 by kneading and melting the propylene-ethylene copolymer and the ethylene-α-olefin copolymer in the presence of 0.05-1 wt.% peroxide and 0.005-0.5 a cross-linking agent.
7. Method according to Claim 6, characterized in that a peroxide inhibitor is also present.
8. Method according to Claim 7, characterized in that the peroxide inhibitor is 1,4-dihydroxybenzene.
9. Method according to any one of claim 6-8, characterized in that the cross-linking agent is 1,4-

dihydroxybenzene.

10. Moulded part containing the cross-linked polymer composition according to any one of Claims 1-7.

11. Car bumper containing the cross-linked polymer composition according to any one of Claims 1-7.

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/NL 95/00441

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L23/10 C08L23/04 C08K5/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,32 30 516 (MITSUBISHI PETROCHEMICAL) 24 March 1983 see page 7, line 3 - page 9, line 22; claim 1 see page 14, line 34 - page 16, line 34 ---	1-11
X	DATABASE WPI Section Ch, Week 8505 Derwent Publications Ltd., London, GB; Class A17, AN 85-028507 XP002001086 & JP,A,59 223 740 (MITSUI PETROCHEMICAL) see abstract --- -/--	1-3,6, 10,11

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
19 April 1996	29.04.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Goovaerts, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Internat l Application No
PCT/NL 95/00441

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 8624 Derwent Publications Ltd., London, GB; Class A17, AN 86-152561 XP002001087 & JP,A,61 085 462 (IDEMITSU PETROCHEM) , 1 May 1986 see abstract	1-3,6,10
A	WO,A,88 08865 (NORSOLOR) 17 November 1988 see claims 1,7,9,13	1-11

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interna... al Application No
PCT/NL 95/00441

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A-3230516	24-03-83	JP-C-	1679201	13-07-92
		JP-B-	3043291	02-07-91
		JP-A-	58162619	27-09-83
		JP-A-	58187412	01-11-83
		JP-A-	58032616	25-02-83
		JP-A-	58103548	20-06-83
		US-A-	4454306	12-06-84
WO-A-8808865	17-11-88	FR-A-	2614897	10-11-88
		AT-T-	117341	15-02-95
		AU-B-	617321	28-11-91
		AU-B-	1724088	06-12-88
		CA-A-	1317057	27-04-93
		DE-D-	3852783	02-03-95
		DE-T-	3852783	20-07-95
		EP-A-	0294253	07-12-88
		ES-T-	2067482	01-04-95
		JP-T-	3503422	01-08-91
		US-A-	5334663	02-08-94
		US-A-	5218046	08-06-93